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THE DEPENDENCE OF η ON LINE BREADTH OF THE
SPECTRAL LINE R(4) OF HYDROGEN FLUORIDE

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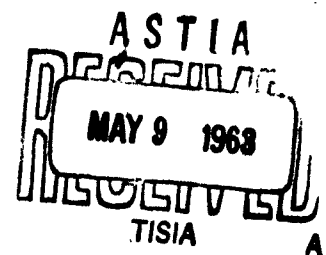
THE DEPENDENCE OF η ON LINE BREADTH OF THE SPECTRAL LINE

R (4) OF HYDROGEN FLUORIDE

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

Hugo A. Hardt, LT, USN

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CHAPTER I

INTRODUCTION

The infrared spectrum of molecules is investigated in order that the physicist may learn more about intramolecular and intermolecular forces. The first involves properties of the isolated molecule while the latter involves those properties which give rise to the spectral line breadth. The spectral line shape is also a property of the long and short range forces, the paths, and the velocities of molecules colliding with one another. The purpose of this work is to study one of the properties of spectral line shapes, namely η, a quantity defined on page 20.

One observes experimentally that spectral lines are not sharp but have a spread or breadth about a central point or line center. This spread depends on various parameters, including the pressure of the absorbing gas. In the pressure range in this study, this spread was found to be approximately proportional to the pressure, or equivalent, to the collision rate. It has been found convenient to write an expression for the spectral line in terms of the absorption coefficient, α, which is related to the fractional transmission, T, by the expression

$$T = e^{-\alpha L}$$

where L is the path length. It has also been found that the spectral line shape may then be represented by the Lorentz expression

1

$$\alpha = \frac{\alpha_0 \, (\Delta \nu)^2}{(\nu - \nu_0)^\pi + (\Delta \nu)^2}$$

the parameters of which will be fully described later. It is sufficient for continuity to point out that the absorption coefficient, and thus the spectral line shape, has a fundamental dependence upon frequency.

The sources of spectral line broadening are:

1. Natural Broadening. This type of broadening is always present and depends on the internal structure of the molecule. It may be interpreted classically as due to radiation damping, or quantum-mechanically as due to the Heisenberg Uncertainty Principle. A limitation to the time a molecule spends in an energy level results in an uncertainty of that level, which in turn results in an uncertainty in frequency absorbed. Since the average lifetime is large, the uncertainty in the energy is small, and thus the line breadth is small. Natural broadening is negligible compared with the widtn due to other causes.

2. Doppler Broadening. Broadening of this sort occurs when a molecule has a velocity component parallel to the direction of propagation of the radiation being absorbed. The molecules of the gas being investigated have a Maxwellian distribution of velocities, and thus the breadth will vary with the square root of the temperature divided by the molecular weight. For the pressures used in this work, the Doppler effect is completely masked by pressure broadening.

3. Pressure Broadening. Disturbances due to interactions between molecules are the cause of pressure broadening. It is sometimes called collision broadening when the collision time is short compared

with the time between collisions and the molecules involved are sufficiently far from other molecules to be considered as free. In this case, the collision may be considered as binary. Pressure broadening is the main cause of broadening in the pressure range in this study.

4. <u>Statistical Broadening</u>. This type of broadening is actually pressure broadening where the pressures are high enough that molecules may not be considered free. At high pressures, the molecules are always under the influence of intermolecular interactions, even though these may be weak, and the frequency absorbed depends on the amount of interaction occurring when absorption occurs. The term statistical broadening is not applied to the range of pressures used in this experiment.

5. <u>Instrumental Broadening</u>. Instrumental broadening has nothing to do with molecular interactions, but is due entirely to the finite width of slits, imperfections in the optics of the spectrometer, and the diffraction patterns of the optics. This leads to a discrepancy between the measured shape of a line and its true shape. The measured line appears to be more intense in the wings and less intense in the center than the true line. One may correct for this effect by using a method developed at The University of Tennessee. This correction is necessary only at low pressures.

6. <u>Temperature</u>. Temperatures play an important role in the shape of spectral lines. A change in temperature will affect most of the types of broadening mentioned above. This work was performed at a constant temperature (100°C), and thus no change was observed or expected.

In the continued study of spectral line shapes being performed at the Physics Department at The University of Tennessee, it was desired to study lines that would readily yield information. These lines should be intense and far apart. The lines should be intense in order that the lines be fairly sharp at low pressures and far enough apart to prevent too much contribution from adjacent lines for the pressures, temperature, and path lengths used. Investigators at The University of Tennessee have found that hydrogen fluoride (HF) is ideally suited to fit these requirements. It also has the added advantage of being a diatomic molecule which simplifies theoretical calculations. However, HF has many undesirable chemical properties. It is very reactive at STP, and there are strongly absorbing spectral lines due to water vapor in the region of the spectrum in which HF was investigated. However, techniques and equipment have been developed in the Physics Department of The University of Tennessee and at the Oak Ridge Gaseous Diffusion Plant which permit the study of HF.

The infrared spectrum of hydrogen fluoride has been extensively examined at The University of Tennessee and at the Oak Ridge Gaseous Diffusion Plant. The work up to 1956 was well described by Kuipers (1). Since then Kuipers (1), Smith (2), and others have shown that HF may be readily handled. Herget et al. (3) measured the line positions and determined the line shapes of many of the lines in the fundamental band. They also determined many of the line positions in the first overtone. The effects of polymer absorption and foreign gas broadening were studied by D. F. Smith (2). The line positions of many of the

pure rotational lines were determined by Mason (4).

Herget et al. found that the Lorentz expression for the shape of a pressure broadened line was found to fit the true line shape quite well if the power η of the distance from the line center was allowed to vary. He found that the power varied from an average of 1.85 for wide lines to an average value of 2.0 for narrow lines. He also concluded that the change of η did not depend upon pressure but appeared to depend upon the half-absorption half-width ($\sigma \gamma$), which is the distance in wave numbers, from line center (cm^{-1}) to where the per cent absorption is one-half the maximum per cent absorption. The aim of this investigation was to determine where this change of η takes place for a specific line, R (4), for various $\sigma \gamma$.

CHAPTER II

EXPERIMENTAL DETAILS

I. THE SPECTROMETER

The high resolution, vacuum-grating spectrometer at The University of Tennessee has been described adequately by Herndon and Nielsen (5). Various modifications and additions to the spectrometer, which have improved the resolution and thus increased the usefulness of the spectrometer, have been described by Herget et al. (3). The following equipment was used to obtain the data for the thesis:

A Bausch and Lomb grating (6.5 in. x 8.75 in.) with 15,240 lines ruled per inch, used in first order,

A germanium band pass filter passing about 80 per cent of the radiation between 2.0μ and 2.8μ, substituted for the prism monochromator,

An Eastman Kodak uncooled Ektron lead sulfide detector, operating into a 13 cps Perkin-Elmer chopper-amplifier system,

A Kinney pump to evacuate the tank, housing the spectrometer, to a pressure of about 40μ, and

Various baffles introduced to minimize stray light.
Under these conditions, the spectrometer is easily capable of resolving lines separated by 0.1 cm^{-1} at 4000 cm^{-1}.

II. THE ABSORPTION CELL

The absorption cell used in this work was 9.78 cm in length and was constructed of brass. The window holder is shown in Figure 1. HF reacts slightly with brass but soon surface fluorides are formed which prevent further reaction.

This experiment was done in cooperation with L. Eldreth (6) who had originally planned to examine the temperature dependence of the line shape parameters (α_0 and $\Delta \gamma$). Since temperatures beyond the melting point of teflon would necessarily be required, it was decided that metal O rings would be used to obtain a seal between various components of the cell. These O rings were of stainless steel tubing 0.094 inches in diameter with 0.006 inch walls. They were pressure filled and were plated with 0.002 inches of gold. An effective seal could not be obtained, and this part of the experiment was abandoned. Teflon gaskets were then used, and an effective seal obtained.

Sapphire cell windows were used in this experiment since they transmit most of the 2.5 μ radiation without the appearance of "window bands" and since they resist HF corrosion sufficiently well at moderate pressures.

The cell was mounted on a selsyn-driven rack and pinion which allowed the cell to be raised from or lowered into the infrared beam from outside the spectrometer tank.
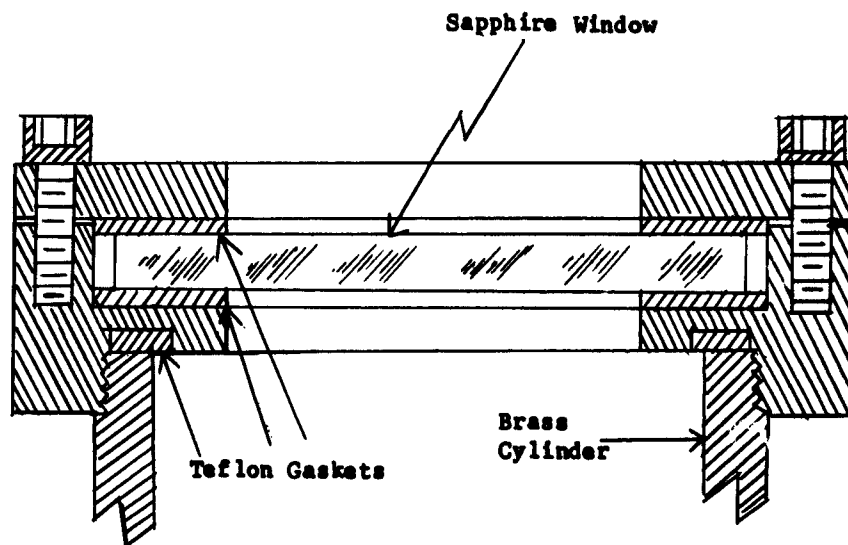
An identical holder screws to the other end of the cylinder.

Figure 1. The window holder for the 9.78 cm cell.

III. PRESSURE AND TEMPERATURE MEASUREMENTS

Hydrogen fluoride was introduced into the cell at proper pressures by using the gas handling system described by Herget et al. (3). The system is constructed of monel, nickel, and stainless steel. Some of the more important pieces of equipment are:

A Taylor Differential Pressure Transmitter which accurately measures up to 128 cm pressure,

A Bourdon gauge, equipped with a monel Bourdon tube, used for rough measurements, usually above 128 cm pressure, and

A Hastings thermocouple gauge used to measure vacuum.

Vacuum in the spectrometer tank was measured by using a Hastings thermocouple gauge and a Bourdon vacuum gauge, the vacuum gauge being used for initial rough measurements.

The temperature of the sample cell was maintained by a calrod heating element wrapped around the cell and connected to a variac located outside the tank. The manifold and the gas handling system components were heated with strip heaters and asbestos-covered heating wire. The temperature of the cell was measured with a Leeds and Northup thermocouple-potentiometer system. The thermocouple wire was iron-constantan matched by Leeds and Northup to $\pm$ 0.02°C. The experiment showing that measuring the temperature of the outside surface of the cell gave an accurate measurement of the temperature of the gas in the cell when the cell was in a vacuum was described by Eldreth (6).

IV. INTERPRETATION OF THE DATA

The experimental results of the investigation of the infrared region of hydrogen fluoride are in the form of curves drawn by the machine on chart paper. The following items are read from the chart paper and are necessary in the determination of the results:

Zero Line - The position on the chart paper corresponding to zero per cent transmission or 100 per cent absorption,

Base Line - The position on the chart paper corresponding to 100 per cent transmission or zero per cent absorption, and

Line Value - The position on the chart paper of the curve drawn during the experiment.

These values are illustrated in Figure 2. The line value was read directly from the chart paper at equal, small intervals, measured along the chart.

The zero line was obtained by recording the value of the line value near line center at high pressures, where the absorption was essentially 100 per cent. It was observed that this value was a constant. The base line was determined by scanning the portion of the spectral regions to be investigated with no HF in the sample cell. The resulting curve is the zero per cent absorption curve and was found to be a straight line. Consequently, only a reading at the beginning and end of the spectral region was required. A simple calculation, performed by the computer, gave the value of the base line for each interval.
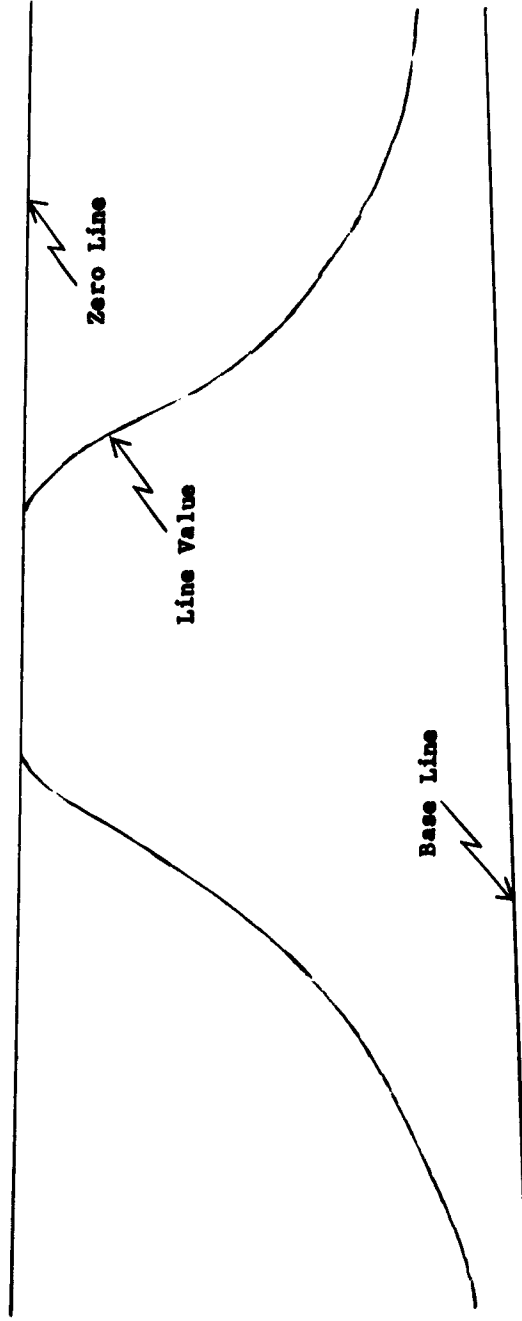
Figure 2. Typical absorption curve showing the zero line, the base line, and the line value.

Spectral lines measured at low pressures require a correction for instrumental broadening. The correction is called "slit function correction" and has been described by Herget et al. (3). Since there was a possibility that a slit function might be required, Dr. N. M. Gailar and Mr. Van McCombs, of The University of Tennessee, rewrote the slit function computer program in order that it may be used in FORTRAN II programming. The spectral lines observed in this work required no slit correction and thus the program was not used.

The method for determining the value of $|\gamma - \gamma_0|$ was one in which the chart paper was used as a "ruler". The method, along with the determination of its accuracy, is described as follows. The cm^{-1} difference between two consecutive HF lines was divided by the number of chart units separating them. This gave a value of cm^{-1} per chart unit, averaged over the interval. The number of cm^{-1} per chart unit was used to find the value of several distances from line center in cm^{-1}. This was done by counting the number of chart units and then multiplying by the number of cm^{-1} per chart unit. These distances from line center were also found by using the formula

$$\gamma = \frac{K}{\sin \theta}$$

where K is the grating constant and θ is the distance from central image. In the spectral region covered in this experiment, the difference between the two methods was found to be less than the accuracy of measurement. Thus it was determined that the method of using chart units was suitable.

V. OVERLAPPING OF SPECTRAL LINES

The contributions of adjacent spectral lines to the per cent absorption of a spectral line were determined using the following method. The value of the absorption coefficient, α, of adjacent lines in the spectral region examined was found by use of the Lorentz expression

$$\alpha = \frac{\alpha_0 \, (\Delta \gamma)^2}{(\gamma - \gamma_0)^\eta + (\Delta \gamma)^2}$$

where α_0 is the maximum value of the absorption coefficient and is measured at line center (γ_0), and the quantity $\Delta \gamma$ is the Lorentz half-width of the spectral line and is equal to $\left| \gamma - \gamma_0 \right|$ measured where α is equal to one-half α_0. The values of α_0, γ_0, and $\Delta \gamma$ were those determined by Herget et al. (3). For this determination, the value of η was taken to be 1.8. A slight variation of this value did not appreciably change the size of the correction. The contribution of the absorption coefficients of adjacent lines was found to be nearly a straight line in the desired spectral range and thus only the value of the end points were necessary.

VI. COMPUTER PROGRAM

The R (4) line of hydrogen fluoride observed at low pressures sometime requires a slit correction, depending on the pressure. As a result, the author became familiar with computer programming. As a direct result of being familiar with programming, it was apparent that all the data obtained could be processed from start to finish entirely by the computer. A program was written for this purpose and is shown in Appendix A. The reference in the program to "slit correction made"

is the slit correction program developed by Dr. N. M. Gailar and Mr. Van McCombs of The University of Tennessee. Various switches are available on the IBM 1620 Computer that allow the operator to include or exclude certain parts of a computer program. If the data are first processed by the slit correction program, the results are used in the processing program with switch 1 on. If the slit correction is not necessary, as was the case in all the curves investigated, the data are fed directly into the processing program with switch 1 in the off position. The computer language demands that data be identified to the computer by code names. For this program, the required input data, along with their computer names, were as follows:

Values of the base line	TOP
End points of the zero line	BASEA and BASEB
End points of the α correction for adjacent lines	ALPA and ALPB
Value of α_0	ALPO
Pressure	P
Path length of the cell	PL
Number of values of the line value	N

The spectral lines were drawn on the chart paper in such a manner that the direction toward the right was the direction of increasing angle from central image. The values of BASEA and ALPA were taken on the left-hand side of the curve and the values of BASEB and ALPB were taken on the right-hand side of the curve. The processing program provided the following information:

1) per cent absorption (not corrected for adjacent lines)

2) absorption coefficient, α (corrected for adjacent lines)

3) square root of $((\alpha_0 - \alpha)/\alpha)$

4) $\ln ((\alpha_0 - \alpha)/\alpha)$

Item 3 is plotted against the chart units and determines the line center (Figure 3). Item 4 is plotted against the logarithm of the distance from line center, $\ln \left| \nu - \nu_0^2 \right|$, and the slope of the resulting line is the value η (Figure 4). Table I is the values of items 1, 2, 3, and 4 computed for the pressure used in Figures 3 and 4.
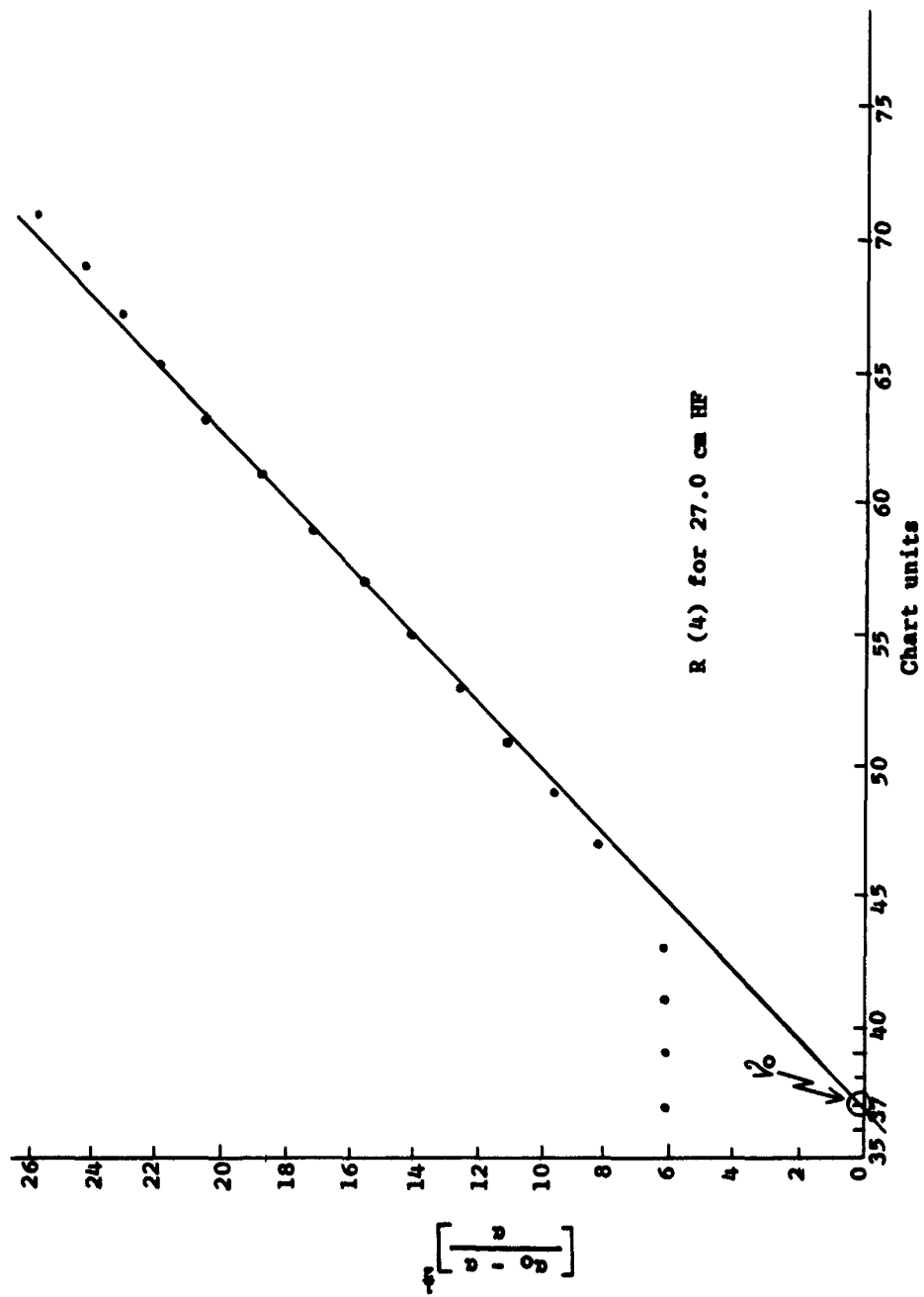
Figure 3. Example of the method of determining line center.

$\eta(\text{slope}) = 2.00$

R (4) for 27.0 cm Hf
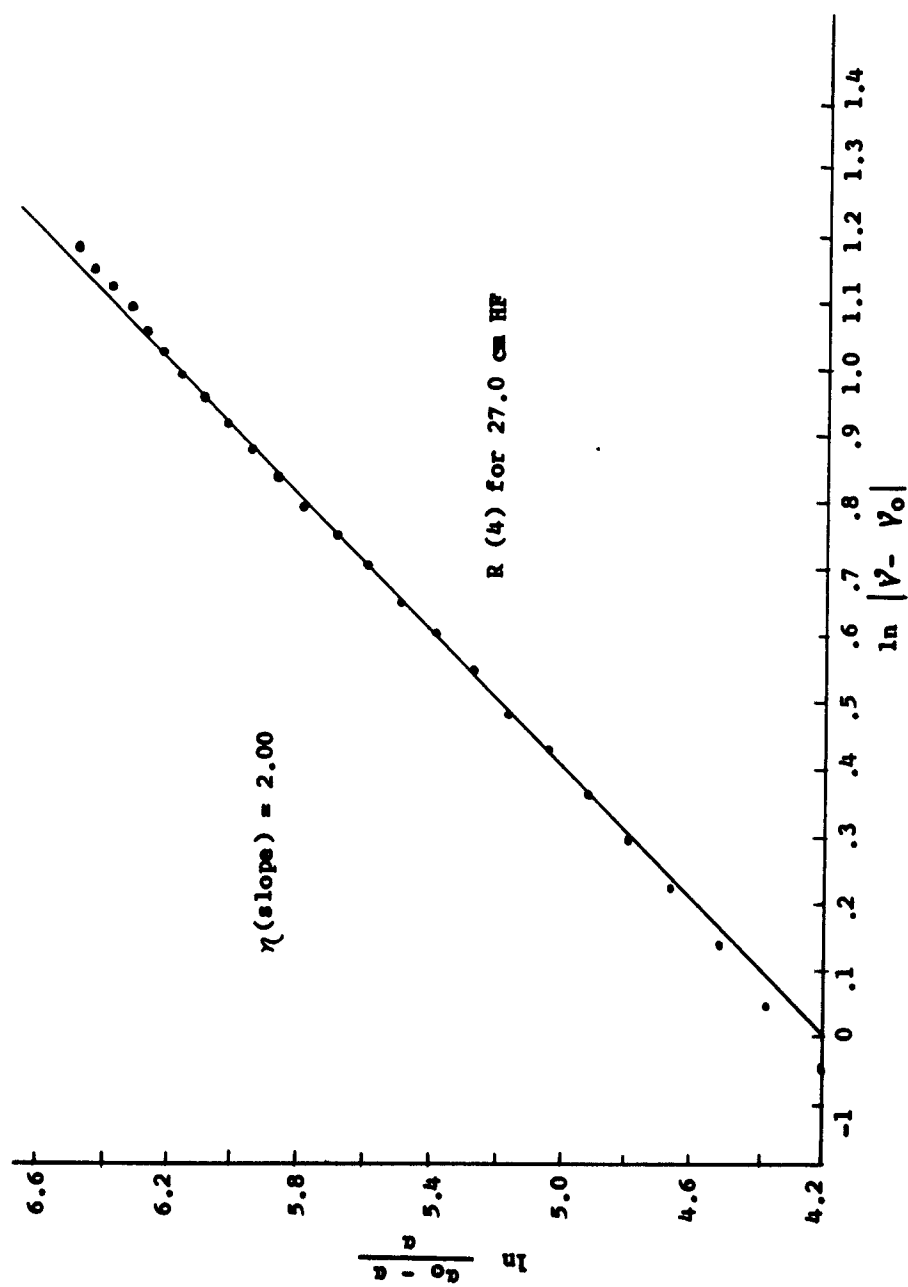
Figure 4. Example of the method of determining the Lorentz exponent, η.

TABLE I

PER CENT ABSORPTION, ABSORPTION COEFFICIENT, ANSA, AND ANSB FOR 27.0 CM OF PRESSURE

Per Cent Absorption	Absorption Coefficient	ANSA	ANSB	Per Cent Absorption	Absorption Coefficient	ANSA	ANSB
21.4	.023	28.4	6.69	100.0	.469	6.2	3.66
22.4	.024	27.6	6.64	100.0	.469	6.2	3.66
23.6	.026	26.8	6.58	100.0	.469	6.2	3.66
24.5	.027	26.1	6.53	100.0	.469	6.2	3.66
26.1	.029	25.2	6.45	100.0	.469	6.2	3.66
27.8	.032	24.2	6.38	100.0	.469	6.2	3.66
29.3	.034	23.4	6.31	99.6	.469	6.2	3.66
30.8	.036	22.7	6.24	98.7	.445	6.4	3.72
32.5	.039	21.9	6.18	96.4	.337	7.4	4.00
34.4	.042	21.2	6.10	93.3	.274	8.2	4.21
36.3	.045	20.4	6.03	89.8	.232	8.9	4.38
38.4	.048	19.7	5.96	85.9	.199	9.6	4.53
40.6	.052	19.0	5.89	81.9	.173	10.3	4.67
42.9	.056	18.3	5.81	77.9	.153	11.0	4.80
45.7	.061	17.5	5.72	73.4	.134	11.8	4.93
48.5	.066	16.8	5.64	69.4	.119	12.5	5.05
51.6	.073	16.0	5.55	65.1	.106	13.2	5.17
55.0	.080	15.2	5.45	61.2	.095	14.0	5.27
58.5	.088	14.5	5.35	57.4	.086	14.8	5.38
62.6	.099	13.7	5.24	53.6	.077	15.6	5.49
67.0	.112	12.9	5.11	50.1	.070	16.4	5.59
71.8	.128	12.1	4.98	46.9	.063	17.2	5.69
76.2	.145	11.3	4.85	43.7	.057	18.1	5.79
80.5	.166	10.6	4.72	40.9	.052	18.9	5.88
85.0	.192	9.8	4.57	38.6	.048	19.6	5.95
89.6	.230	9.0	4.39	36.6	.045	20.4	6.03
93.2	.273	8.2	4.21	34.7	.042	21.1	6.10
96.2	.334	7.4	4.01	32.9	.039	21.8	6.16
98.2	.410	6.7	3.80	31.6	.037	22.4	6.22
99.3	.469	6.2	3.66	30.2	.035	23.0	6.27
100.0	.469	6.2	3.66	28.9	.033	23.7	6.33
100.0	.469	6.2	3.66	27.5	.031	24.4	6.39
100.0	.469	6.2	3.66	26.3	.030	25.1	6.45
100.0	.469	6.2	3.66	25.1	.028	25.8	6.50
100.0	.469	6.2	3.66	24.1	.027	26.5	6.55
100.0	.469	6.2	3.66	23.1	.025	27.2	6.60
100.0	.469	6.2	3.66	22.1	.024	27.9	6.66

CHAPTER III

RESULTS AND CONCLUSIONS

I. EXPERIMENTAL RESULTS

The IBM 1620 computer at The University of Tennessee Computing Center was used to perform all the calculations required in this work. The values, for each curve, of TOP, BASEA, BASEB, ALPA, ALPB, ALPO, P, PL, and N, described in the Computer Program section of Chapter II, were fed into the computer along with the Computer Program listed in Appendix A. The computer calculated the following for each point on the curve.

1) Per Cent Absorption (ABS) = $\dfrac{\text{Distance from base line to line value x 100}}{\text{Distance from base line to zero line}}$

2) Absorption Coefficient = $\dfrac{0 - \ln (1 - \frac{ABS}{100})}{\text{Path Length}}$.

3) ANSA = $\sqrt{\dfrac{\alpha_0 - \alpha}{\alpha}}$

4) ANSB = $\ln \left(\dfrac{\alpha_0 - \alpha}{\alpha} \right)$

The values of the per cent absorption of the spectral line R (4) for each pressure are listed in Appendix B. The values of the per cent absorption are taken one chart unit or 0.09567 cm^{-1} apart. The line center for each curve was found by plotting ANSA as a function of chart units. The intercept of the straight line drawn through these points is the line center. Figure 3 is a typical example of the described method.

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The value η from the Lorentz formula for the absorption coefficient

$$\alpha = \frac{\alpha_0 \, (\Delta \nu)^2}{(\nu - \nu_0)^\eta + (\Delta \nu)^2}$$

was determined in the following manner. The correspondence between chart units and distance from line center (in cm^{-1}) was calculated. The value of $\ln |\nu - \nu_0|$ was calculated for each point, and a plot of ANSB as a function of $\ln |\nu - \nu_0|$ was made for each curve. A best straight line was fitted to each curve and the slope of each line calculated. Note that the curves are not necessarily straight lines at either end. The reason is that small errors in the regions greater than 80 per cent and less than 20 per cent absorption become large errors in the values of ANSB. As a result, the curves deviate from the straight line in these regions. The plot of ANSB as a function of $\ln |\nu - \nu_0|$ is shown in Figure 4. The value of the slope of the line is the value η, the coefficient in the Lorentz formula. Finally a plot of η as a function of $d\nu$, the half-absorption half-width, is illustrated in Figure 5.

The plot of ANSB as a function of $\ln |\nu - \nu_0|$ also yields information about the Lorentz half-width $(\Delta \nu)$. The intercept of the straight line with the line drawn through $\ln |\nu - \nu_0| = 0$ gives the value corresponding to $-2 \ln (\Delta \nu)$. Figure 6 is a graph of the value of $\Delta \nu$ as a function of pressure.
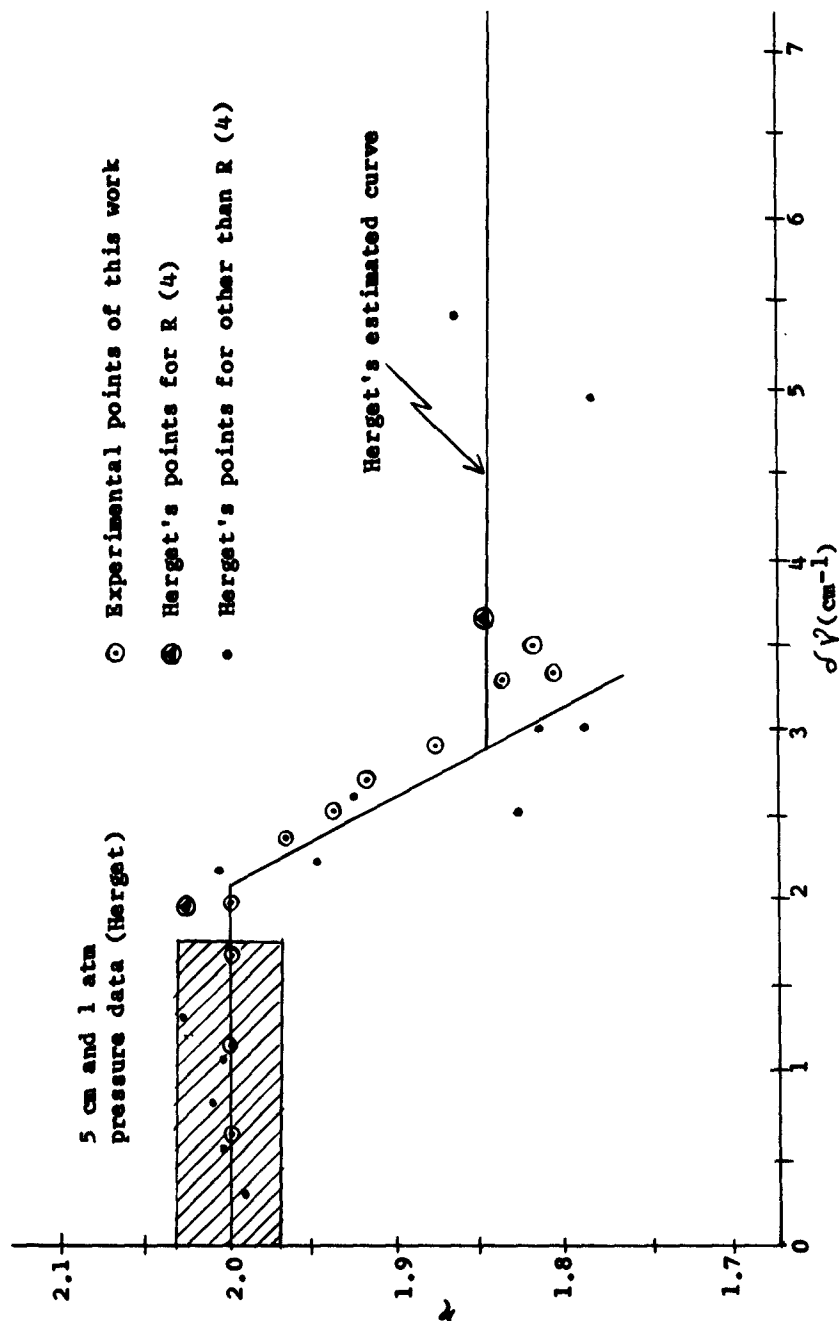
Figure 5. Dependence of the Lorentz exponent, χ, on the half-absorption half-width, $\delta\gamma$.
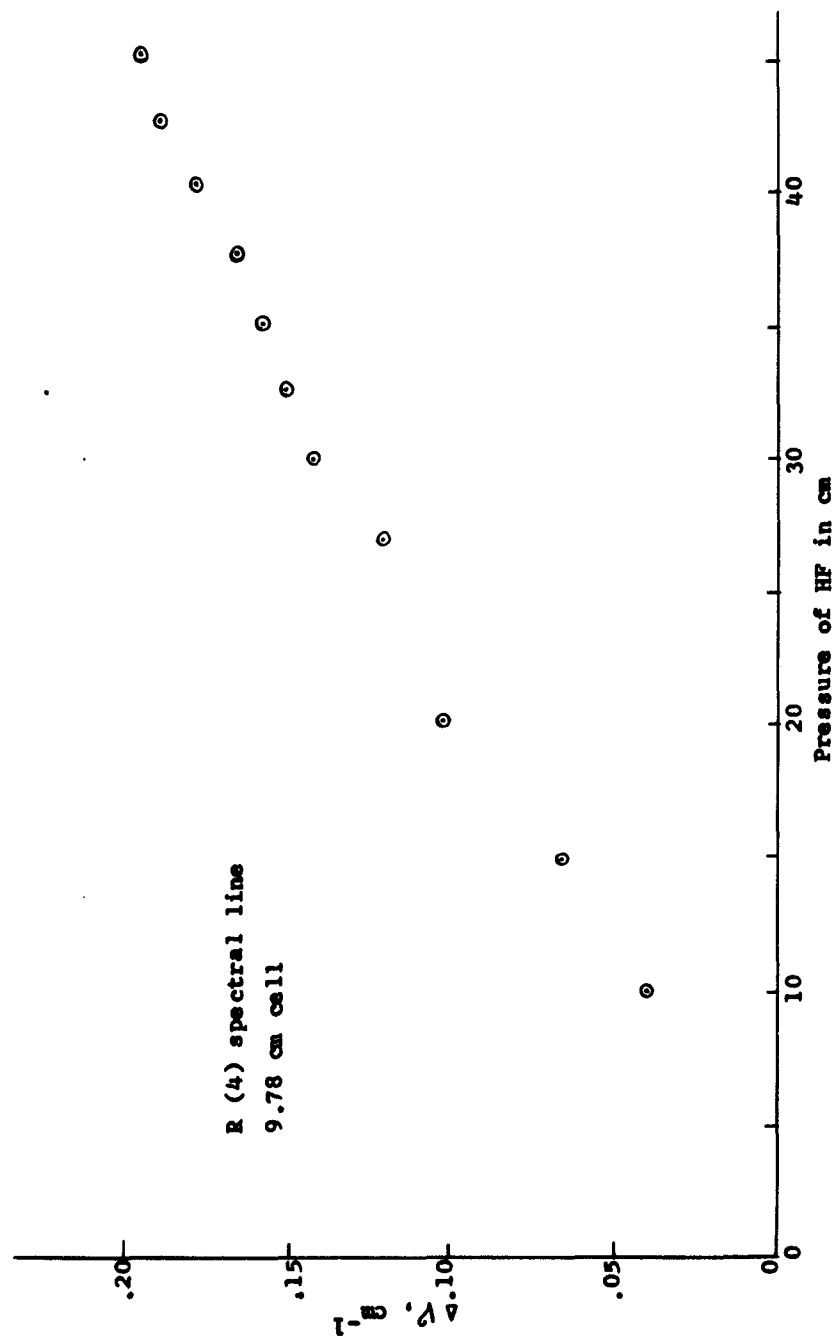
Figure 6. Dependence of the Lorentz half-width, $\Delta \nu$, on pressure.

II. CONCLUSIONS

Herget et al. (3) found that the Lorentz expression for the shape
of a pressure broadened curve fitted the true line shape quite well if
the power η of the distance from line center was allowed to vary. He
found that the Lorentz exponent, η, appeared to depend on the half-
absorption half-width, $\delta\nu$. He also found that η was dependent on the
distance from line center, $\left| \nu - \nu_0 \right|$. His determinations were based on
evaluations of many lines at pressures of 5 cm, 50 cm, 1 atm, and 5
atm.

This work was performed on one spectral line, R (4), for many
pressures. From the results obtained, it may be concluded that the
Lorentz exponent is a function of the distance from line center. It
must be pointed out that Herget was correct in his conclusion that the
dependency appears to be on the half-absorption half-width, $\delta\nu$. The
connection between $\delta\nu$ and $\left| \nu - \nu_0 \right|$ is that η is measured over a very
short range of $\left| \nu - \nu_0 \right|$ which centers about $\delta\nu$. In this very small
region, η appears to be a constant and thus appears to be dependent
upon $\delta\nu$. The values of η for various pressures and corresponding
$\delta\nu$'s are listed in Table II and are accurate to $\pm$ .03. This value
of accuracy was obtained by evaluating the maximum and minimum slope of
the curves.

The graph of η plotted as a function of $\delta\nu$ is shown in Figure 5.
In addition to showing the points obtained in this work, the figure also
shows the results obtained by Herget. Both results agree remarkably

TABLE II

LORENTZ EXPONENT FOR VARIOUS PRESSURES OF HYDROGEN FLUORIDE

Pressure (cm)	$\delta \gamma$ (cm^{-1})	Lorentz Exponent (η)
10.0	0.65	2.00
15.0	1.17	2.00
20.0	1.73	2.00
27.0	2.01	2.00
30.0	2.40	1.97
32.5	2.55	1.94
35.0	2.75	1.92
37.5	2.92	1.88
40.0	3.30	1.84
42.5	3.35	1.81
45.0	3.50	1.82

well in both the range of variation of χ and in the slope of the result-
ing curve. The fact that there is agreement when one observes many lines
at few pressures (Herget's points) and when one observes one line for
many pressures strongly indicates that the dependence exists in the range
shown. In addition, the fact that changing many parameters yields the
same results strongly indicates that the dependence is on the distance
from line center.

CHAPTER IV

SUMMARY AND SUGGESTIONS FOR FUTURE WORK

I. SUMMARY

The aim of this investigation was to determine experimentally the value of the Lorentz exponent, η, for various half-absorption half-widths of the R (4) spectral line in the hydrogen fluoride fundamental band.

All data were taken on the high resolution vacuum-grating spectrometer at The University of Tennessee. The R (5) line of the first overtone of CO was used to determine a slit correction function but was not used by the author.

The line shapes of R (4) were taken for various pressures, and a determination of the Lorentz exponent was made for each line. The exponent was found to be a function of the distance from line center and was found to vary in the range observed by Herget et al. (3).

II. SUGGESTIONS FOR FUTURE WORK

1. The dependence of the Lorentz exponent upon the half-absorption half-width should be measured for other spectral lines in the fundamental band.

2. The temperature dependence of the Lorentz parameters should be measured.

3. The slit correction function should be tested on several spectral lines for various low pressures.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Kuipers, G. A., J. Mol. Spectroscopy 2, 775 (1958).

2. Smith, D. F., J. Mol. Spectroscopy 3, 473 (1959).

3. Herget, W. F., "The Infrared Spectrum of Hydrogen Fluoride; Line Positions and Line Shapes," Ph. D. Thesis, Department of Physics, The University of Tennessee, Knoxville (June 1962); also J. Opt. Soc. Am. 52, 1108 (1962) and J. Opt. Soc. Am. 52, 1113 (1962).

4. Private communication with author.

5. Herndon, J. A. and A. H. Nielsen, "Design and Construction of a Vacuum-Grating Spectrometer for the Infrared," Technical Report No. 2, Office of Ordnance Research, Department of the Army (December 1957); also J. Opt. Soc. Am. 52, 1108 (1962).

6. Eldreth, L. F., "Infrared Spectrum of Hydrogen Fluoride; Shapes, Positions and Intensities of High J Lines in the Fundamental Band," M. S. Thesis, Department of Physics, The University of Tennessee, Knoxville (December 1962).

APPENDIXES

COMPUTER PROGRAM

```
C       C       HARDT ALPHA PROGRAM
C               SW1 ON ,SLIT CORRECTION MADE
        500     IF (SENSE SWITCH 1) 400,300
                DIMENSION CURV(150)
                DIMENSION ABS(150)
        400     READ 70, ND,P,PL,N,TEST
         70     FORMAT (I4,F12.5,F12.5,I4,F12.5)
                PUNCH 70,ND,P,PL,N,TEST
                DO 10 I=1,N
                READ 21, J,ABS(I)
         21     FORMAT(I4,F14.6)
         10     CONTINUE
                READ22,ALPA,ALPB,ALPO
         22     FORMAT (F10.5,F10.5,F10.3)
                AN=N
                XC=(ALPB-ALPA)/(AN-1.)
                GO TO 401
C               END OF CORRECTED INPUT
C               START OF NON-CORRECTED INPUT
        300     READ 2,ND,TOP,BASEA,BASEB,ALPA,ALPB,ALPO,P,PL,N
          2     FORMAT (I3,F5.2,F5.2,F5.2,F7.5,F7.5,F7.3,F6.2,F5.2,I3)
                READ 3,(CURV(1),I=1,N)
          3     FORMAT (7F10.2)
                AN=N
                XA=(BASEB-BASEA)/(AN-1.)
                XC=(ALPB-ALPA)/(AN-1.)
                PUNCH 73,NP,P,PL,N
         73     FORMAT (I3,F10.2,F10.2,I5)
        401     CONTINUE
                DO 4 I=1,N
                IF (SENSE SWITCH 1) 402,301
        301     DIFF=CURV(1)-BASEA
                TOT=TOP-BASEA
                BASEA=BASEA+XA
                ABS(I)=(DIFF/TOT)*100.
        402     CONTINUE
                Q2=ABS(I)/100.
                IF(Q2-.99)12,12,13
         13     Q1=.99
                GO TO 15
         12     Q1=Q2
```

31

```
15          ALP=0.-LOGF(1.-Q1)/PL
            ALP=ALP-ALPA
            ALPA=ALPA+XC
            IF (ALPA-ALP)27,27,26
26          ANSA=SQRTF((ALPA-ALP)/ALP)
            ANSB=LOGF((ALPO-ALP)/ALP)
    27      PUNCH 8,1,ABS(1),ALP,ANSA,ANSB
     8      FORMAT(13,4X,F10.2,4X,F10.4,4X,F10.4,4X,F10.4)
     4      CONTINUE
            PAUSE
            GO TO 500
            END
```

TABLE III

PER CENT ABSORPTION FOR R (4) SPECTRAL LINES MEASURED AT 100°C IN THE 9.78 CM CELL

Pressure and Value of η	Per Cent Absorption 0.09567 cm^{-1} Intervals			
10.0 cm	8.99	24.60	99.84	34.70
2.00	9.46	27.12	100.00	31.07
	10.09	29.81	100.00	28.70
	10.41	32.96	100.00	25.70
	10.88	36.90	99.84	23.50
	11.51	41.79	99.84	21.60
	11.98	46.68	97.79	20.18
	12.30	52.36	94.16	· 18.76
	12.77	59.46	88.64	17.35
	13.24	66.71	80.75	16.08
	13.72	73.97	73.65	14.82
	14.35	82.17	66.08	14.03
	15.61	88.64	58.99	12.61
	17.19	94.00	52.68	11.82
	18.61	97.00	46.84	11.04
	20.34	98.58	41.95	10.56
	22.39	99.52	38.32	
15.0 cm	20.37	56.46	100.00	56.88
2.00	21.60	60.49	100.00	53.11
	22.82	64.99	100.00	49.49
	24.20	69.65	100.00	46.35
	25.57	74.31	100.00	43.51
	26.80	79.14	100.00	40.83
	28.33	83.80	98.90	38.46
	29.71	88.31	97.02	36.25
	31.40	92.05	94.52	34.03
	33.25	94.85	91.55	31.98
	35.41	97.35	87.94	30.23
	37.72	99.22	83.71	28.33
	40.20	100.00	79.01	26.59
	43.13	100.00	74.31	25.31
	46.23	100.00	69.60	23.88
	49.48	100.00	65.05	22.60
	53.05	100.00	60.81	21.33

TABLE III (CONTINUED)

Pressure and Value of χ	Per Cent Absorption 0.09567 cm^{-1} Intervals				
20.0 cm	26.57	54.62	99.39	99.53	50.35
2.00	27.59	57.02	100.00	97.85	48.01
	28.77	59.58	100.00	96.46	45.97
	29.79	62.29	100.00	94.62	43.94
	30.81	65.30	100.00	92.15	41.90
	31.84	68.62	100.00	89.38	39.86
	33.02	71.64	100.00	86.30	38.13
	34.04	74.82	100.00	83.21	36.55
	35.52	78.45	100.00	79.66	34.98
	37.00	81.93	100.00	76.27	33.40
	38.79	85.26	100.00	73.02	31.82
	40.27	88.14	100.00	69.46	30.54
	42.06	91.03	100.00	66.36	29.27
	43.99	93.46	100.00	63.57	28.00
	45.78	95.43	100.00	60.47	26.88
	48.03	97.10	100.00	57.67	25.91
	50.12	98.78	100.00	55.03	24.95
	52.22	99.08	100.00	52.69	23.98
27.0 cm	21.40	48.48	100.00	96.35	40.91
2.00	22.39	51.63	100.00	93.25	38.64
	23.55	54.97	100.00	89.77	36.56
	24.54	58.50	100.00	85.93	34.65
	26.07	62.56	100.00	81.89	32.92
	27.77	66.99	100.00	77.85	31.57
	29.29	71.78	100.00	73.43	30.21
	30.82	76.23	100.00	69.38	28.85
	32.53	80.50	100.00	65.13	27.48
	34.42	84.96	100.00	61.24	26.30
	36.31	89.60	100.00	57.35	25.12
	38.38	93.18	100.00	53.63	24.12
	40.63	96.23	100.00	50.09	23.12
	42.89	98.20	99.63	46.91	22.12
	45.68	99.28	98.72	43.73	21.12

TABLE III (CONTINUED)

Pressure and Value of η	Per Cent Absorption 0.09567 cm^{-1} Intervals				
30.0 cm	22.70	49.36	100.00	99.53	47.65
1.97	23.53	52.18	100.00	97.99	45.42
	24.51	55.30	100.00	95.67	43.50
	25.35	58.73	100.00	92.73	41.42
	26.48	62.01	100.00	89.94	39.65
	27.77	65.46	100.00	86.68	38.03
	28.91	69.05	100.00	83.42	36.42
	30.35	72.65	100.00	79.84	34.79
	31.94	76.26	100.00	76.41	33.17
	33.53	79.72	100.00	72.36	31.54
	35.27	83.64	100.00	68.45	29.92
	37.02	87.57	100.00	64.69	28.44
	38.92	91.50	100.00	61.08	26.96
	40.82	95.29	100.00	57.47	25.49
	42.72	97.72	100.00	54.79	24.01
	44.93	99.24	100.00	52.10	22.21
	46.99	99.84	99.84	49.88	20.56
32.5 cm	21.89	47.49	99.69	100.00	51.38
1.94	22.58	50.04	100.00	99.34	48.56
	23.55	52.74	100.00	97.38	45.90
	24.53	55.62	100.00	95.40	43.91
	25.37	58.94	100.00	93.24	41.73
	26.50	62.29	100.00	90.08	39.88
	27.91	66.25	100.00	87.05	38.38
	29.33	70.09	100.00	83.83	36.86
	30.90	74.25	100.00	80.59	35.33
	32.33	78.59	100.00	77.32	33.97
	33.92	82.51	100.00	73.85	32.59
	35.52	86.91	100.00	70.19	31.57
	37.13	90.00	100.00	66.84	30.17
	39.03	93.11	100.00	63.11	28.76
	40.81	95.49	100.00	60.05	27.33
	43.02	97.28	100.00	57.12	25.90
	45.11	98.63	100.00	54.18	24.63

TABLE III (CONTINUED)

Pressure and Value of η	Per Cent Absorption 0.09567 cm^{-1} Intervals				
35.0 cm	30.25	67.07	100.00	93.31	46.55
1.92	32.04	70.13	100.00	90.97	44.72
	33.10	73.19	100.00	88.31	43.19
	34.02	76.86	100.00	85.64	41.51
	35.09	80.10	100.00	82.49	39.97
	36.89	83.64	100.00	79.49	38.44
	38.55	87.19	100.00	76.49	37.06
	40.36	90.75	100.00	73.31	35.67
	42.31	94.17	100.00	70.44	34.45
	44.28	95.81	100.00	67.41	33.22
	46.54	97.60	100.00	64.52	32.31
	48.95	99.10	100.00	61.79	31.55
	51.23	99.69	100.00	59.20	30.80
	53.65	100.00	99.53	56.77	29.88
	56.09	100.00	99.07	54.16	28.96
	58.53	100.00	97.98	52.03	28.04
	61.41	100.00	96.74	50.21	27.11
	64.31	100.00	95.34	48.23	26.18
37.5 cm	29.70	59.78	100.00	100.00	59.49
1.88	30.43	62.34	100.00	100.00	57.48
	31.76	64.90	100.00	99.38	55.67
	32.69	67.47	100.00	97.94	53.76
	34.41	70.04	100.00	97.12	51.85
	35.54	73.61	100.00	95.68	49.94
	37.27	77.39	100.00	93.41	48.02
	39.00	80.58	100.00	90.93	46.09
	39.94	83.57	100.00	87.42	44.38
	42.26	87.37	100.00	84.73	42.87
	44.20	90.77	100.00	81.42	41.56
	46.53	92.97	100.00	78.72	40.05
	48.08	95.37	100.00	75.81	38.74
	49.62	97.38	100.00	72.68	37.22
	51.77	97.98	100.00	69.97	35.49
	53.72	98.99	100.00	67.04	34.39
	55.47	99.59	100.00	64.11	33.28
	57.62	100.00	100.00	61.80	32.59

TABLE III (CONTINUED)

Pressure and Value of η	Per Cent Absorption 0.09567 cm^{-1} Intervals				
40.0 cm	31.73	63.85	100.00	100.00	62.60
1.84	32.82	66.85	100.00	100.00	60.33
	34.06	69.86	100.00	99.40	57.91
	35.15	72.87	100.00	98.52	55.93
	36.39	75.88	100.00	96.74	54.10
	37.49	78.90	100.00	94.81	52.11
	39.16	81.92	100.00	92.88	50.57
	40.26	84.80	100.00	90.35	48.73
	41.65	87.69	100.00	87.97	47.19
	43.47	90.29	100.00	85.73	45.80
	45.29	92.60	100.00	83.19	44.41
	47.26	94.77	100.00	80.65	43.01
	49.09	96.66	100.00	77.95	41.76
	51.06	97.96	100.00	75.40	40.36
	53.33	98.98	100.00	72.85	38.96
	55.59	99.85	100.00	70.15	37.70
	58.44	100.00	100.00	67.44	36.60
	61.14	100.00	100.00	65.02	35.49
42.5 cm	33.29	58.82	97.86	100.00	75.51
1.81	34.01	61.04	98.68	100.00	72.91
	34.90	63.43	99.67	100.00	70.65
	35.94	65.98	100.00	100.00	68.39
	36.99	68.38	100.00	100.00	65.94
	38.36	70.78	100.00	100.00	63.50
	39.41	73.35	100.00	99.49	61.39
	40.62	75.92	100.00	98.64	59.10
	41.84	78.50	100.00	97.79	57.15
	43.38	81.25	100.00	96.27	55.03
	44.92	83.68	100.00	94.23	53.07
	46.46	86.27	100.00	92.35	51.46
	48.01	88.55	100.00	90.13	49.84
	49.56	90.83	100.00	87.74	48.57
	51.12	92.62	100.00	85.51	47.12
	53.00	94.09	100.00	82.93	45.67
	54.88	95.56	100.00	80.35	44.39
	56.61	96.87	100.00	77.76	42.93

TABLE III (CONTINUED)

Pressure and Value of η	Per Cent Absorption 0.09567 cm^{-1} Intervals				
45.0 cm	37.10	65.21	100.00	100.00	73.03
	38.09	67.68	100.00	100.00	70.70
	39.07	69.80	100.00	100.00	68.36
	40.59	72.28	100.00	100.00	66.41
	42.11	74.77	100.00	98.87	64.06
	43.10	77.27	100.00	97.74	61.90
	44.10	79.77	100.00	96.79	59.54
	45.45	82.28	100.00	95.84	57.75
	47.16	84.61	100.00	94.71	55.38
	48.70	87.13	100.00	93.00	53.97
	50.24	89.65	100.00	91.09	51.98
	51.96	92.18	100.00	89.19	50.14
	53.69	94.54	100.00	87.28	48.56
	55.42	96.54	100.00	85.36	46.94
	57.33	97.81	100.00	83.25	46.10
	59.07	99.45	100.00	80.75	45.25
	60.99	100.00	100.00	78.06	43.62
	62.92	100.00	100.00	75.55	42.18

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Infrared Spectroscopy

Hardt, Hugo A., and
Gailar, N. M.

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Air Force Cambridge Research Laboratories, Bedford,
Mass. Geophysics Research Directorate.

THE DEPENDENCE OF η ON LINE BREADTH OF THE
SPECTRAL LINE R(4) OF HYDROGEN FLUORIDE, by
Hardt and Gailar. March 1963. 38 pp.

AFCRL-63-262. Unclassified Report

This report is a study of the variation with pressure
of the true line shape of R(4) in the HF band. A modi-
fied Lorentzian line shape in which the exponent was
found to be only a function of the distance from line
center fitted the experimental points. The change in
exponent from η = 2 to η = 1.83 occurs in the interval
of 2 cm^{-1} to 3 cm^{-1} from line center.